

Highly magnetic core-shell graphene coated Fe/Co nanoparticles

Maria Sarno^{1,2}, Claudia Cirillo¹, Massimiliano Polichetti^{2,3} and Paolo Ciambelli^{1,2}

¹ Department of Industrial Engineering, ² Research Centre NANO_MATES, ³ Department of Physics

University of Salerno, via Giovanni Paolo II, 134, 84084 Fisciano, Italy

msarno@unisa.it

Introduction. Graphene coated magnetic nanoparticles (GCMNP) are object of a lot a research addressed to improve chemical and thermal stability and biocompatibility of magnetic nanoparticles (MNPs), in view of the exploitation of their properties in different applications including catalytic, environmental, biological, biomedical and electronic. Carbon covering has many advantages over other coatings, such as much higher chemical and thermal stability, easy functionalization. Typically, a two step process (MNP synthesis and then coating) is performed, however producing GCMNPs in a single step is a fascinating challenge [1]. Among different strategies suggested to prepare MNPs, Chemical Vapor Deposition (CVD) is the easiest one to be scaled up towards an economically viable production [2]. In fact, little attention has been devoted to the effect of process parameters in the preparation of stable MNPs, to obtain a quality controlled product and this is even more rare for GCMNPs. For a given catalyst and carbon source the CVD products strongly depend of the operating conditions and the selective and controlled coating process is still to be understood and optimized. Moreover, little attention has been devoted to investigate the influence of the support on the GCMNPs characteristics. Finally, insight into the formation mechanism is a critical issue to improve the control of the synthesis process. Herein, we report the preparation of stable core-shell graphene-coated magnetic nanoparticles (GCMNPs) via Catalytic Chemical Vapor Deposition (CCVD) of methane at atmospheric pressure. The magnetic properties of the nanoparticles have been also investigated.

Materials and methods. The Co, Fe catalyst (50 wt.% of each metal) was prepared by wet impregnation of gibbsite (γ -Al(OH)₃) powder [3]. The experimental plant for the synthesis was equipped with on-line analyzers (Uras 26, ABB) that permit the monitoring of the inlet and outlet reactor concentrations of the reactants. To characterize the reaction products various techniques were employed as follows: transmission electron microscopy (TEM) (FEI Tecnai electron microscope operating at 200 kV), scanning electron microscopy (SEM) (LEO 1525 microscope), Raman spectroscopy ((Renishaw inVia; 514 nm excitation wavelength), thermogravimetric analysis (TG-DTG) (SDTQ 600 Analyzer (TA Instruments)) coupled with a quadrupole mass detector, X-ray diffraction analysis (Bruker D8 X-ray diffractometer) and N₂ adsorption-desorption at 77 K.

Results The change of process parameters: total flow rate, hydrocarbon methane partial pressure and catalyst weight in the synthesis process, has shown that the selective covering of nanoparticles and the control of the coating thickness can be obtained by feeding the hydrocarbon in a suitable carrier, preventing the unwanted homogeneous decomposition and increasing the conversion of methane.

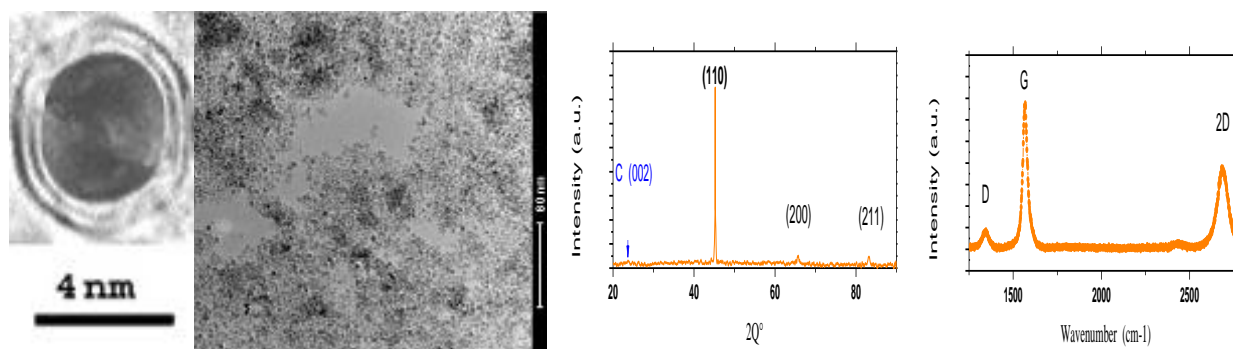


Figure 1. TEM images of nanoparticles covered by 1-2 layers graphene. X-ray diffraction patterns and Raman Spectrum of GCMNPs.

The best result, consisting of nanoparticles covered by two graphene layers and free of other carbon species is shown in Figure 1. The nanoparticles have an average diameter of 4.12 nm with a 0.86 nm standard deviation, as measured for ~400 nanocrystals) and are covered by 1-2 layers of graphene (see the HRTEM in the Figure 1). In Figure 1, the X-ray diffraction pattern of GCMNPs is also shown. The peaks at 44.87°, 65.32° and 82.75° are typical of a crystalline body-centered-cubic Co/Fe alloy. It is important to note the absence of the (002) diffraction peak due to the stacking of AB graphite. In the Raman spectrum of GCMNPs the most prominent features of the sp² carbon materials, which are

known as the G band and the G' or 2D band, were observed at 1582 cm^{-1} and approximately 2700 cm^{-1} , respectively, using 514 nm excitation wavelength. The thermal stability was investigated by thermogravimetric analysis in flowing air, finding the nanoparticles are stable up to 350°C . The X-ray diffraction analysis after three weeks was found to be identical to that shown in Figure 1.

To understand the mechanism of the carbon coverage, the concentrations of CH_4 , C_2H_2 , C_2H_4 and H_2 in the effluent stream have been monitored during the nanoparticles synthesis via on-line analyzers. The relevant profiles are shown in Figure 2. The methane conversion and hydrogen yield were calculated by assuming that the methane conversion to carbon and hydrogen was the primary reaction: $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$. The agreement between the CH_4 conversion (x_{CH_4}) and the H_2 yield (R_{H_2}) curves (Figure 2) confirms that the catalyst resulted in the selective formation of carbon and hydrogen. The evolution of the concentration profiles of the exhaust gases in the presence of non-impregnated gibbsite indicates a lack of methane decomposition in the absence of the catalysts in these operating conditions. Starting with the hydrogen produced from the catalytic decomposition of methane during the GCMNP1 test, the total deposited carbon was calculated to be 7.5 mg , which corresponds to a mean deposited carbon mass of 0.025 mg/sec a very close to the saturation threshold limit for the Co/Fe alloy, $\text{gC/gFeCo} = 0.45\text{ at.}\%$ at 800°C corresponding to 0.026 mg of carbon. Therefore, after the formation of GCMNPs during the pretreatment step, carbon saturation was achieved in approximately 1 sec . After 1 sec , carbon begins to cover the nanoparticle via carbon supersaturation and continuous precipitation from the cluster to form the graphitic structure. When the reaction was terminated, the catalyst remains active, and the carbon coverage phenomenon terminates when complete coverage of the GCMNP is achieved resulting in inactivation of the metal. The residual carbon mass inside the GCMNPs, which precipitated during the cooling phase, will contribute to the complete coverage of the metal [2]. It is important to note that there is no methane conversion in the absence of the metal catalyst on the support.

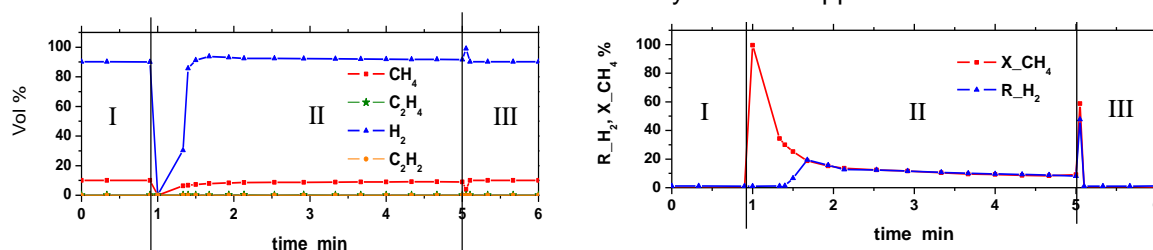


Figure 2. On line analysis and CH_4 conversion and H_2 yield during GCMNPs synthesis.

In Figure 3 we present the hysteresis loops of the nanoparticles at $T = 5\text{ K}$ and $T = 300\text{ K}$. A saturation magnetization of 230 e.m.u./g for the sample, the highest M_s obtained for nanocrystal, can be measured. The presented hysteresis loops, are coherent with a superparamagnetic behavior..

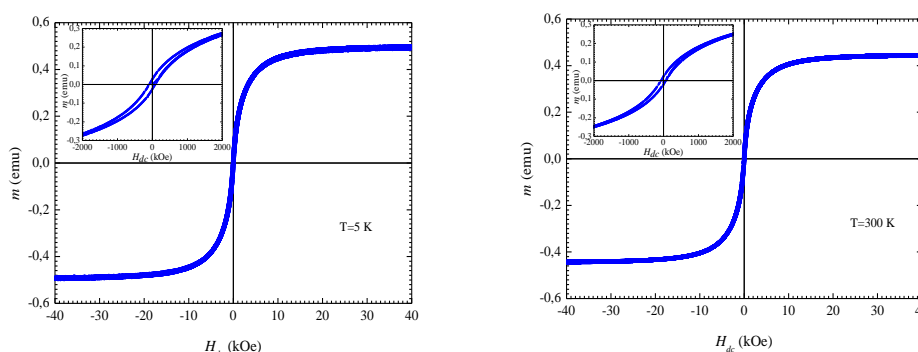


Figure 3. Magnetic hysteresis loops at $T=5\text{K}$ and 300 K for GCMNPs.

Conclusion. Stable core-shell graphene-coated GCMNPs have been prepared by CCVD. Monodispersed 4.1 nm diameter body-centered-cubic-FeCo nanoparticles are coated by 1-2 layers of graphene. An M_s value of 230 e.m.u./g has been measured for the graphene-coated nanoparticles

References

1. A.H. Lu, E.L. Salabas, F. Schüth, *Angew. Chem. Int. Ed.*, 46 (2007) 1222-1244.
2. W.S. Seo, J.H. Lee, X. Sun, Y. Suzuki, D. Mann, Z. Liu, M. Terashima, P.C. Yang, M.V. Mcconnell, D.G. Nishimura, H. Dai, *Nat. Mater.* 5 (2006) 971–976.
3. M. Sarno, D. Sannino, C. Leone, P. Ciambelli, *J. Mol. Catal. A-Chem.* 357 (2012) 26-38.